# Reactivity and Characterization of Coal Macerals

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In a study of the organic structures in coals and their reactivity in chemical and thermal processes, it is desirable to reduce the complexity of the material with some sort of physical separation. One such approach is the separation of the coals into their maceral groups, which are the microscopically identifiable organic portions of coal which have different origins, chemical and physical features, and reactivity. Two bituminous coals have been separated into their three main maceral groups: exinite, vitrinite, and inertinite, using a modified float-sink technique which uses analytical density gradient centrifugation (DGC) to determine the appropriate density ranges. The DGC technique which exploits the differences in densities has just recently been reported (1,2).

The chemistry of macerals separated by DGC, float-sink and hand picking has been investigated recently by several techniques including: solid ^{13}C nmr (3,4), oxidation (5,6), and mass spectrometry (5,6,7,8). Early work focused on chemical properties (9) and esr spectroscopy (10). In the approach taken in this study the maceral concentrates were pyrolyzed in a vacuum and the resulting products collected and then characterized by gas chromatography mass spectrometry and by GC microwave plasma emission spectroscopy. The vacuum technique was chosen over the typical on-line pyrolysis-GCMS method for two reasons. First, experiments in this laboratory have shown that with the vacuum technique, secondary reactions such as aromatization of alicyclics is less likely to occur. Second, better quantitative data can be obtained with a batch type reaction scheme.

In addition to characterization of thermal products, the chemical reactivity of these concentrates has been studied. Reactive hydrogens such as benzylic types have been determined from the reaction of the macerals with pyridine and iodine to form pyridinium iodides:

$$\text{Coal-ArCH}_2^- \xrightarrow[\text{I}_2]{\text{pyridine}} \text{Coal-ArCH-} + \text{HI} \qquad\qquad 1)$$
$$\underset{\text{Py}^+\text{I}^-}{|}$$
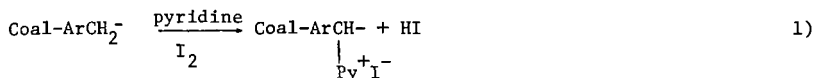
It has been shown that the number of pyridinium iodides per 100 carbon atoms in the original coal decreases with increasing rank (11). Further studies have shown that these derivatized coals are activated toward oxidative solubilization using a reagent, alkaline silver oxide, which normally is quite ineffective in dissolving raw coals. In the results from the thermal and chemical reactions, similarities and differences have been noted which will be discussed later. Also, it should be emphasized that in this study we are examining maceral concentrates from the three main groups which are derived from the same coal. These coals were chosen to be representative of bituminous coals and not to be sapropelic coals where the chemistry may be more unusual due to the typically large exinite content.

EXPERIMENTAL

Two of the coals used in this study were obtained from the Penn State Coal Sample Bank. They were an HVA bituminous coal (PSOC 1103) from the Upper Elkhorn #3 seam in Eastern Kentucky and an HVA bituminous coal (PSOC 828) from the Brazil Block seam in Indiana. A third coal from which vitrinite and fusinite were hand picked was an Illinois No. 2 seam HVC bituminous coal from Northern Illinois. All

of the elemental analyses, petrographic analyses, and yields of the samples are presented in Table 1. The details of the sink-float technique have been reported previously (1). Typically, 3 micron particle size demineralized coal is centrifuged in aqueous $CsCl_2$ solution of the appropriate density with a small amount of surfactant added to disperse the coal particles. The exinites in the float are collected and the sink fraction is further separated into vitrinite and inertinite fractions by repeating the procedure at a higher density. The process yielded gram quantities of concentrates. The density cutoff points were determined from analytical DGC of coals of similar origin and rank. The technique used for petrographic analysis has also been reported earlier (2).

In the pyrolysis experiment, typically 30 mg of sample was heated in a quartz tube at $400^{\circ}C$ for 24 hrs at 2×10^{-3} torr. Tars were trapped at room temperature and the more volatile products at liquid nitrogen temperature. These two fractions were analyzed by GCMPES (MPD-850) using a 25m x 0.25 mm i.d. OV-101 fused silica column and by GCMS (Kratos MS25) using a 30m x 0.25 mm i.d. DB-5 column.

The pyridinium iodide coals were prepared by refluxing 1 g of coal or maceral concentrate in 60 ml of pyridine with 4 g of iodine for 70 hrs. The reaction mixture was poured into 10% aqueous $NaHSO_3$ and the solution filtered. The derivatized coal was washed free of pyridine, dried, and analyzed. Portions of the activated coal were oxidized with freshly prepared silver oxide in refluxing aqueous NaOH. The oxidation products, which were soluble in alkaline solution, were acidified and then extracted with a series of organic solvents. The major products were only soluble in alkaline solution or polar solvents.

RESULTS AND DISCUSSION

Of particular interest in this study is the nature of the non-aromatic structures, in the three main maceral groups. It should be noted that the exinites in both these coals are 90% sporinite. It has been theorized that small molecules, especially the aliphatics, are fairly mobile at some period during the formation of coal (5,6). The studies which support this theory were done on coals that were very rich in exinites and some contained alginite. The two coals chosen in the present work have a more normal distribution of macerals and yet the pyrolysis results indicate that migration of molecules from the exinites to vitrinite and then incorporation into the macromolecular structure might have occurred.

Chromatograms from the GCMPES carbon channel of the tars from two exinites and a vitrinite are shown in Figure 1. Long chain normal alkenes and alkanes dominate the compounds in the tar along with a series of triterpenes which are slightly altered hopanes. A general structure for hopane is shown in the upper right of the figure. Several points should be made concerning these results. First, we believe that these compounds were derived from the macromolecular structures in these macerals. During the preparation of the concentrates most of the soluble molecules are removed. Evidence for this is found from examination of the extracts of the whole, untreated coals. One of the major compounds isolated is the biomarker pristane which has been identified many times previously in extracts (11) and coal liquids (12). However, this compound is absent from the pyrolysis products, although it is stable under the conditions used. At least a portion of the macromolecular structures in the exinite and vitrinite could be similar. As one would expect, the yields of these aliphatic and alicyclic compounds are less in the vitrinites. The yields follow inversely the fraction of aromatic carbons (4) in these three maceral groups. The exinite concentrate for the Kentucky coal is quite impure (50% vitrinite) which is reflected in the pyrolysis yields.

Another similarity between vitrinite and the exinite is the existence of 5 member ring triterpenes in the pyrolysates. These compounds, which show the base peak at m/z = 191 in their mass spectra, have been found in pyrolysis MS of alginite

(5), coal extracts (6,13), and oil shales (14) and are usually associated with some type of algal origins. It is surprising that they were found in these coals and probably more importantly, that they were not aromatized. From the GCMS it appears that only one of these peaks may represent a species containing one aromatized ring. Again these results suggest that there could have been a significant amount of molecular mobility during the early stages of the formation of this coal.

There is a much larger variation between pyrolysis product volatile fractions for the exinites and vitrinites. The sporinite yielded mostly normal alkanes and alkenes up to approximately C19 with C16 being the most abundant product. The very low molecular weight hydrocarbons such as methane and ethane were not analyzed. Also, benzene and phenol derivatives were found as minor products. The vitrinite products were dominated by aromatics such as alkylbenzenes, alkylnaphthalenes, phenols, and naphthols. The smaller alkane/alkenes were also found. These results are more consistent with what was found in pyrolysis MS of sporinites and vitrinites (5,7).

Pyrolysis results for the inertinite concentrates are fairly inconclusive due to the high concentration of vitrinite except for the Ill #2 fusinite which was quite unreactive. Pyrolysis MS of this fusinite shows mostly alkylated naphthalenes and phenanthrenes. What may be interesting is the Kentucky inertinite fraction which is thought to contain ~50% pseudo-vitrinite. This maceral which is usually categorized with vitrinites was placed in the inertinite column due to its low reactivity both in pyrolysis and in the pyridine-iodine reaction.

In the formation of the pyridinium salts the vitrinites were the most reactive and gave similar results to those found for a series of vitrinite rich coals of various ranks. If the sporinites had a highly cross linked aliphatic structure similar to that found in Type I or Type II oil shale kerogens one would expect these exinites to be unreactive. However, they have been found to be only slightly less reactive than vitrinite. Apparently, the yields in this reaction cannot explain the difference in reactivity between sporinites and vitrinites in pyrolysis and SCT liquefaction (15), but do reflect the lower reactivity of inertinites.

A tentative conclusion is that sporinites and vitrinites of the same rank have very similar structures but vary in the mix of aliphatics and aromatics while the structures in inertinites are very different.

ACKNOWLEDGEMENTS

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TABLE I. Sample Characterization and Reaction Yields

| Sample | Elemental Analysis (DMMF %) | | | | | | Maceral Composition | | | Vacuum Pyrolysis Yields | | | Pyridine/I_2 Yields | | Ag$_2$O Oxidation |
	C	H	N	S	O[1]	Ash	Exinite %	Vitrinite %	Inertinite %	Volatiles	Tar	Char	Wt % Increase 100 C	Py$^+$I$^-$/ 100 C	Solubles (Wt%)
Indiana (PSOC 828) Brazil Block															
Whole	74.3	5.9	1.5	1.0	17.3	<1.0	15.1	61.8	23.1	29.6	8.4	62.0	23.4	3.1	48.4
Exinite[2]	78.6	7.5	1.1	1.6	11.2	<1.0	91.0	9.0	~0	23.3	48.4	28.3	19.4	2.6	59.0
Vitrinite	76.4	5.6	1.5	0.9	15.6	<1.0	4.0	89.8	6.2	16.3	16.9	67.8	24.8	3.3	60.3
Inertinite	77.1	5.0	1.3	0.7	15.9	<1.0	0.0	62.5	32.5	16.9	13.4	69.7	19.4	2.6	45.5
Kentucky Upper Elkhorn #3 (PSOC 1103)															
Whole	72.0	5.6	1.4	2.3	18.7	<1.0	7.4	74.2	18.4	12.2	24.5	63.3	28.6	3.8	50.3
Exinite[2]	80.9	6.4	1.5	1.1	10.1	<1.0	45.5	49.6	4.9	14.8	35.2	50.0	25.8	3.4	41.5
Vitrinite	80.4	5.6	1.8	1.0	11.2	<1.0	2.5	92.5	5.0	20.2	22.7	57.1	28.8	3.9	62.5
Inertinite	70.9	3.8	1.2	8.8	15.3	?	1.5	16.2	82.3[3]	8.3	5.9	85.9	14.1	1.8	45.8
Illinois No. 2															
Whole	73.1	5.3	1.3	2.2	18.1			88.6					37.5	5.0	
Vitrinite	73.9	5.3	1.1	1.6	18.1	<1.0		>95		18.3	5.4	76.3			
Inertinite[4]	79.3	3.2	.5	4.0	13.0	4			>90	10.7	1.8	87.5			

[1]By difference; [2]Mostly sporinite; [3]Contains 49.8% pseudo-vitrinite; [4]Mostly fusinite, hand picked; pyrolysed at 500°C.
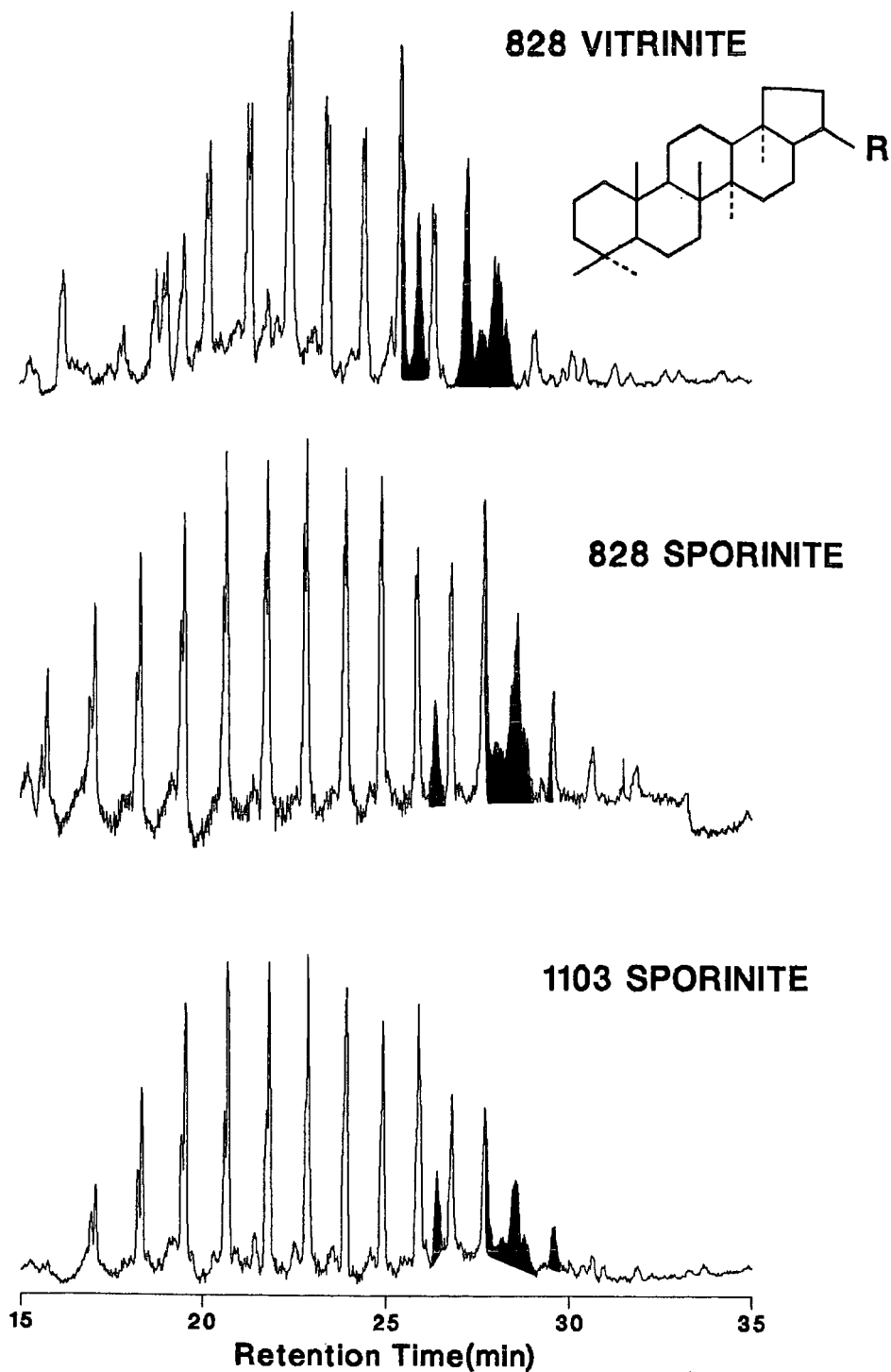
Figure 1. Partial gas chromatograms of vacuum pyrolysis tars. The shaded peaks are compounds derived from triterpenes.